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INVESTIGATION OF MULTIQUANTUM
RELAXATION IN HC1

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INVESTIGATION OF MULTIQUANTUM RELAXATION IN HCl

Second Quarterly Report

During the past quarter progress has been made in three important
areas: (1) the apparatus has been tested and calibrated, and several
preliminary experiments have been performed, (2) various computations
have displayed the degree of sensitivity of $HCl(\nu = 1)$ and $HCl(\nu = 2)$ to
the mechanism of de-excitation, and (3) the reactions:

$$H + HCl(\nu = 3) \rightarrow H_2 + Cl \tag{1}$$

and
$$H + HCl(\nu = 2) \rightarrow H_2 + Cl \tag{2}$$
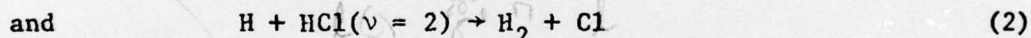
have been studied with some precision. In addition much useful information
on the overall $HCl(\nu)/H$ system has been acquired through conversations
with Dr. J. Wolfrum of the Max-Plank-Institut für Strömungsforschung,
Göttingen.

The optical and electronic layout of the apparatus in its final form
is shown in Fig. 1. Chemiluminescence from the reactor passes through a
sapphire window and is focused by a CaF_2 lens onto the entrance slit of
a small fast monochrometer. Radiation emerging from the exit of the mono-
chrometer is refocused onto a liquid N_2 cooled InSb PV detector. The
signal from this detector, after amplification, is fed into a phase
sensitive detector. The reference for this is obtained from the chopper
wheel mounted immediately adjacent to the flow reactor. In some experi-
ments, the monochrometer is replaced by one of a set of interference
filters chosen so as to isolate a single vibration-rotation band. The

experimentally measured bandwidths (30% of maximum transmission) of
the various filters are shown in Fig. 2. For comparison, the spectra of
HCl is included on this figure. It is clear that filter 1 isolates the
HCl(1 $\rightarrow$ 0) band, and that filter 3 isolates the HCl(3 $\rightarrow$ 2) band. In
order to isolate HCl(2 $\rightarrow$ 1), filter 2 is used in conjunction with an
HCl cold-cell that completely absorbs all radiation in the HCl(1 $\rightarrow$ 0) band.
The apparatus described above has been used in a number of preliminary
experiments. Unfortunately, wall deactivation of HCl(ν) is proving to be
a troublesome interference, and recent experiments have been directed
towards finding wall coatings that are relatively inert to vibrationally
excited HCl.

Computation has shown that HCl($\nu = 1$) is particularly sensitive to
the choice of de-excitation model. This is illustrated in Fig. 3. For
this computation, $(H)_o$ was chosen as 3×10^{13} cm^{-3}, and $(Cl_2)_o$ as
6×10^{12} cm^{-3}. The rate constant for the reaction, $H + Cl_2 \rightarrow HCl + Cl$,
was assumed to be that measured by Niki et al.[1]; namely, 3.5×10^{-11} cm^3
molecule^{-1} sec^{-1}, and the initial vibrational distribution of HCl was
assumed to be that measured by Polanyi and coworkers[2]; namely
$f_o : f_1 : f_2 : f_3 : f_4 = 0 : 0.28 : 1.00 : 0.92 : 0.08$. Three different
deactivation mechanisms were investigated:

(a) a mechanism containing only single quantum transitions,
that is, the reaction

$$H + HCl(\nu) \rightarrow H + HCl(\nu') \tag{3}$$
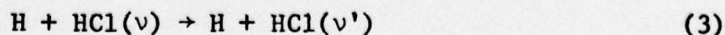
occurred with $\nu = \nu' \pm 1$;

(b)   a mechanism with all transitions ($\nu \rightarrow \nu'$) occurring, and being

equally probable; and

(c)   a mechanism containing only transitions to $\nu' = 0$.

The deactivation rate constants were chosen to conform with the measure-

ments of Wolfrum and Arnoldi[3] for deactivation of $HCl(\nu = 2)$ and $HCl(\nu = 1)$.

The total rate of deactivation of $HCl(\nu = 3)$ was assumed to be three times

that for $HCl(\nu = 1)$. Wall deactivation was assumed to be slow. As can

be seen from Fig. 3, the three different mechanisms are easily distin-

quishable if the concentration of $HCl(\nu = 1)$ is measured. $HCl(\nu = 2)$

is not so sensitive to the deactivation mechanism as can be seen from

Fig. 4.

Reactions (1) and (2) were not included in the above computations

because recent measurements in this laboratory have shown them to be of

little importance in this system. These measurements were a continuation

of those described in the first quarterly report. The method used was

identical to that described in the previous report, except that measure-

ments were made at higher pressures in order to reduce the possibility

of wall de-excitation of $HCl(\nu)$. A careful analysis of our results

showed that less than 15% of the total deactivation of $HCl(\nu = 3)$ and

$HCl(\nu = 2)$ by atomic hydrogen occurred via reactions (1) and (2).

During the last three months, I have visited the laboratories of

Dr. Jurgen Wolfrum at Göttingen, and have spoken to him further at the

Combustion Symposium which was held August 21-25 at M.I.T. He has

continued his studies of the $HCl(\nu)/H$ system that were described in

Chemical Physics Letters in 1974[3], and has several new results that

bear on the research performed under this contract. His main findings

are listed below:

(a) <u>Activation Energy for $HCl(\nu = 1) + H \rightarrow HCl(\nu = 0) + H$</u>

For this reaction, he has measured the rate constant over the tem-
perature range 220-400 K, as:

$$k = 1.32 \times 10^{-10} \exp(-1600 \text{ cal/RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

This activation energy is a little higher than that obtained by Brown,
Glass and Smith in their preliminary experiments.

(b) <u>Rate constant for $HCl(\nu = 2) + H \rightarrow$ products</u>

The rate of total deactivation was measured at 295 K as

$$k = (2.5 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

(c) <u>The Exchange Reaction, $D + HCl(\nu = 1) \rightarrow DCl + H$</u>

Less than 10% of the total deactivation of $HCl(\nu = 1)$ occurred via
exchange. This finding is to be expected in view of the high barrier
to exchange found by Endo and Glass.[4]

(c) <u>The Reaction $H + HCl(\nu = 1) \rightarrow H_2 + Cl$</u>

The rate of this reaction was measured as less than 1.33×10^{-13}
$\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 295 K. Thus excitation of HCl to $\nu = 1$ increases
the rate of this reaction by less than a factor of 4.[5] This observation
is consistent with that described earlier in the report; namely, that
excitation of HCl to $\nu = 2$ or $\nu = 3$ does not greatly increase the rate
of this reaction.

REFERENCES

1. D. H. Stedman, D. F. Steffenson and H. Niki, Chem. Phys. Lett.,
    $\underline{7}$, 173 (1970).

2. K. G. Anlauf, D. S. Horne, R. G. MacDonald, J. C. Polanyi, and
    K. B. Woodall, J. Chem. Phys., $\underline{57}$, 1561 (1972).

3. D. Arnoldi and J. Wolfrum, Chem. Phys. Lett., $\underline{23}$, 234 (1974).

4. H. Endo and G. P. Glass, Chem. Phys. Lett. (in press).

5. J. E. Spencer and G. P. Glass, J. Phys. Chem., $\underline{79}$, 2329 (1975).

FIGURE CAPTIONS

Fig. 1: Diagram of apparatus.

Fig. 2: Measured bandwidth of various interference filters as compared
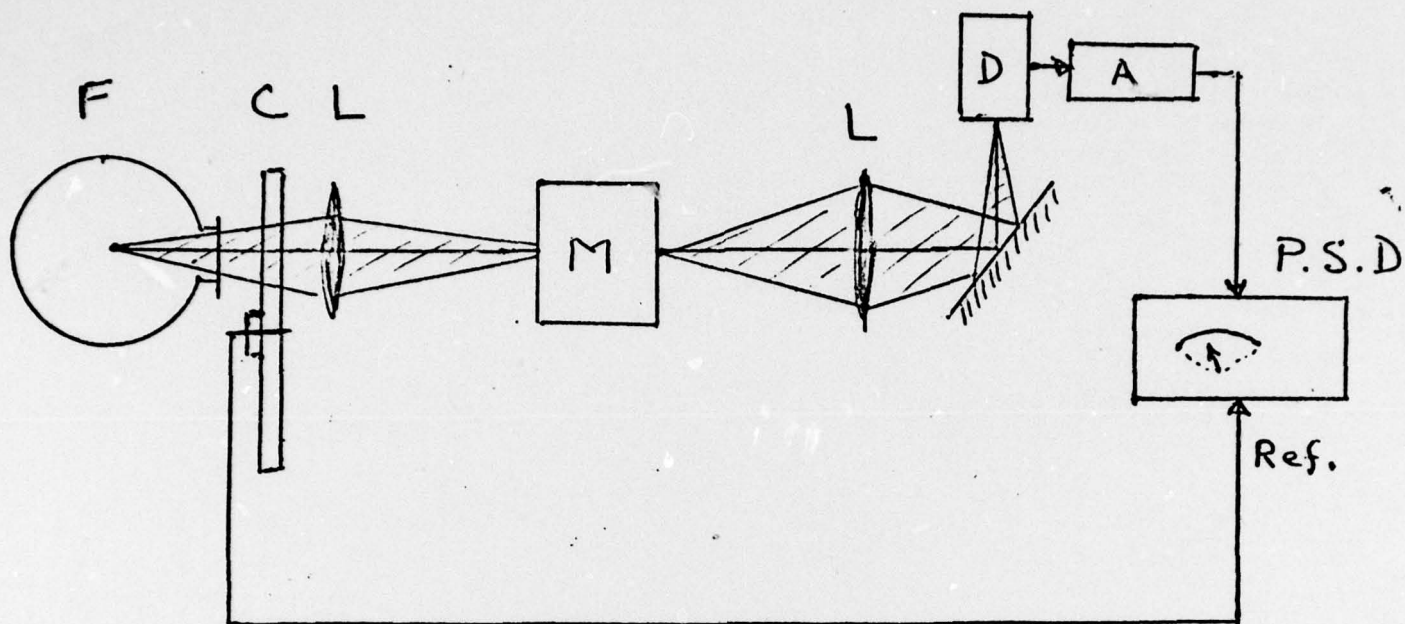   to the HCl emission spectra.

Fig. 3: The concentration of $HCl(\nu = 1)$ vs. reaction time computed
         using three difference deactivation mechanisms. The abscissa
         is given as a fraction of $(Cl_2)_o$. For comparison purposes
         the $HCl(\nu = 3)$ concentration, which is invarient to mechanism,
         is included.

Fig. 4: The concentration of $HCl(\nu = 2)$ vs. reaction time.

F = Flowtube reactor

C = Chopper wheel

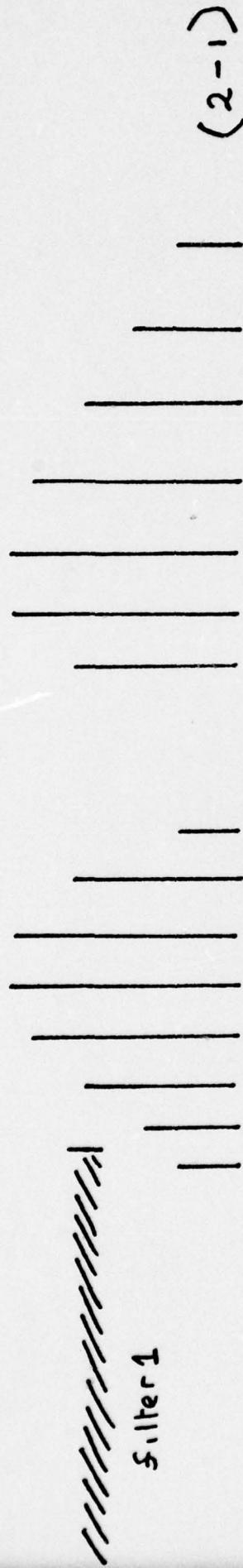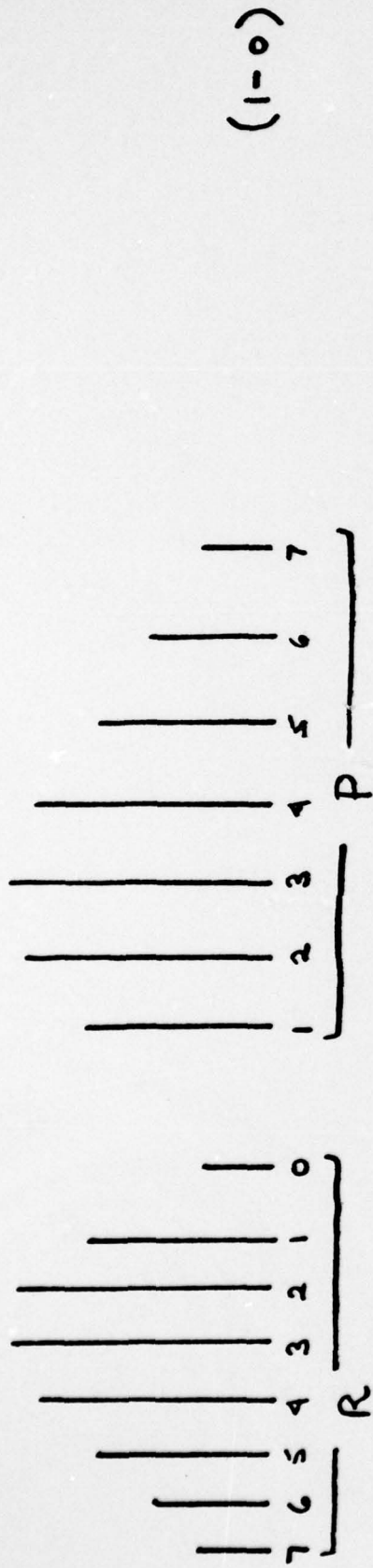L = 1" dia, 50 mm F.L CaF$_2$ lens

M = f/3.7 Monochromator

D = Indium Antimonide, PV, detector

A = Amplifier
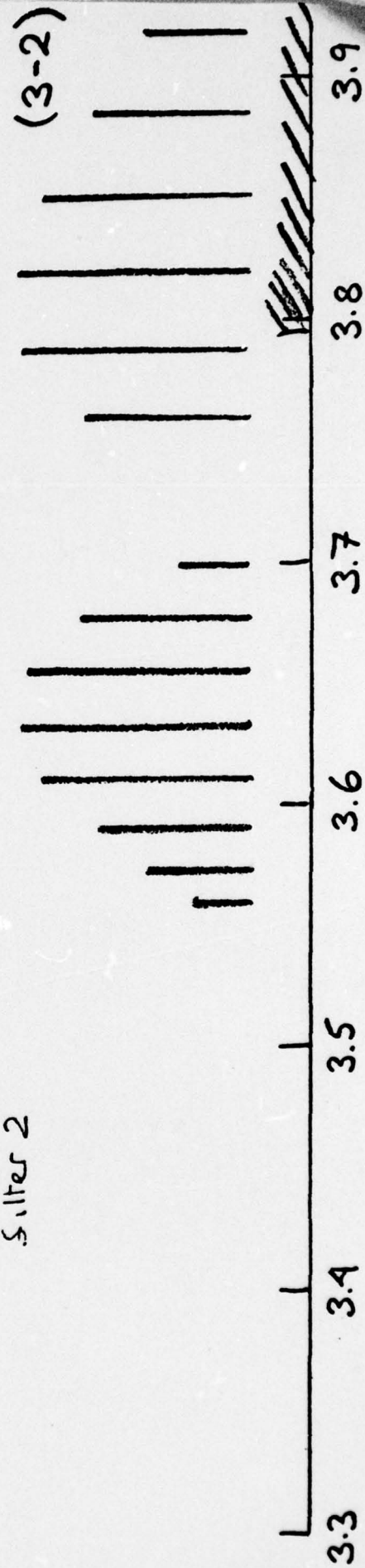
P.S.D. = Phase Sensitive Detector

HCl Spectra

(1-0)

(2-1)

(3-2)
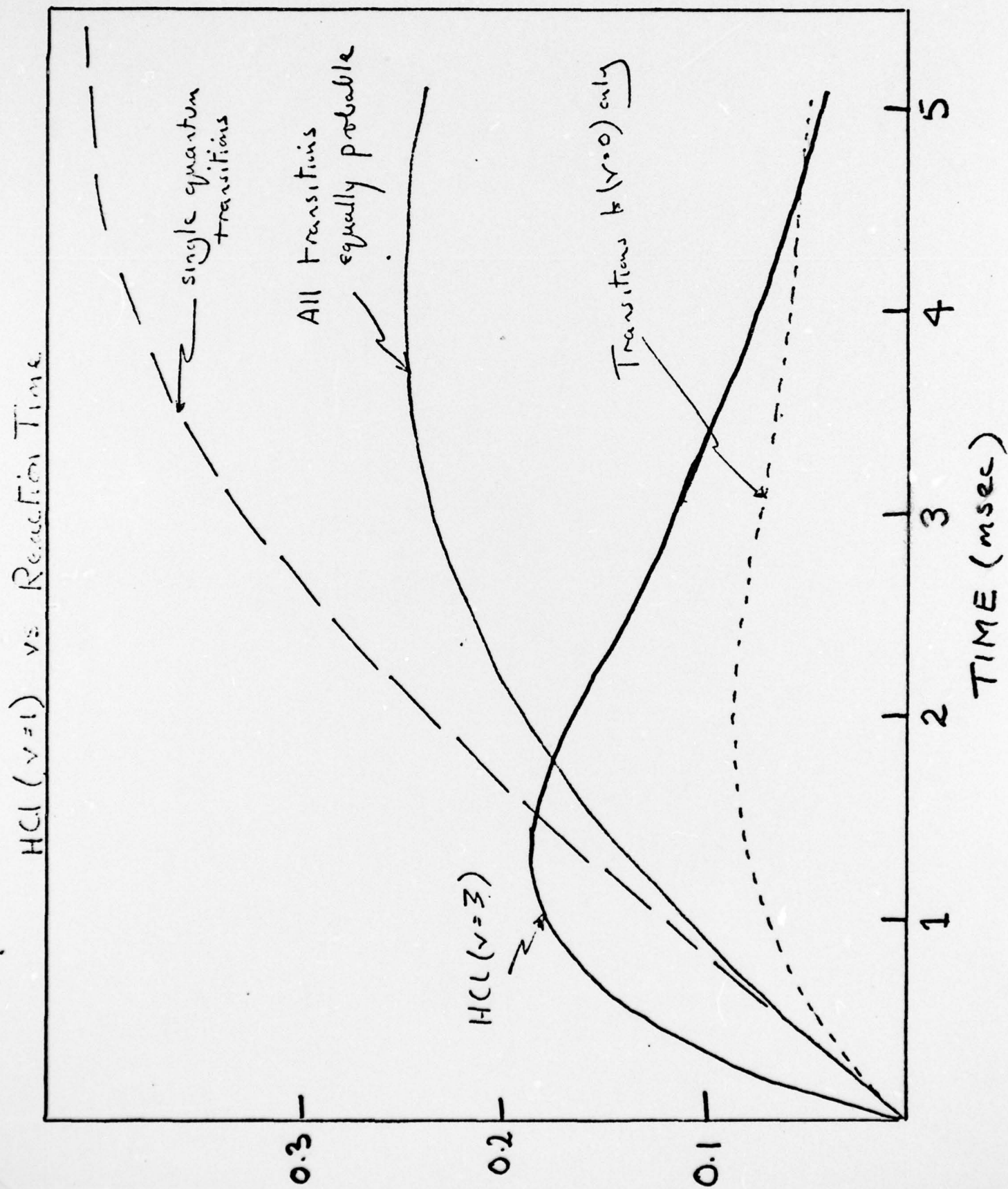
R

P

7 6 5 4 3 2 1 0

7 6 5 4 3 2

Filter 1

Filter 2

Filter 3

3.3   3.4   3.5   3.6   3.7   3.8   3.9

Wavelength (μ).

HCl (v=1) vs Reaction Time.

single quantum transitions

All transitions equally probable

Transitions to (v=0) only

HCl (v=3)

TIME (msec)

0.3
0.2
0.1

HCl (v=2) vs Reaction Time

Single quantum transitions

All transitions equally probable

transitions to (v=0) only.

HCl (v=3)

TIME (msec)

0.3

0.2

0.1

1   2   3   4   5